AMBIENT WATER QUALITY MONITORING PROJECT PLAN

FOR THE

DEPARTMENT OF ENVIRONMENTAL QUALITY

OFFICE OF WATER QUALITY ASSESSMENT

Commonwealth of Virginia
Department of Environmental Quality
Water Quality Assessment
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QUALITY ASSURANCE PROJECT PLAN
FOR THE
DEPARTMENT OF ENVIRONMENTAL QUALITY
OFFICE OF WATER QUALITY ASSESSMENT

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EPA Region 3

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DIVISION OF CONSOLDATED LABORATORY SERVICES

Dr. Tom York

A.4 PROJECT/ TASK ORGANIZATION

Figures 1 and 2 depict the organizational structures of the Department of Environmental Quality and Division of Consolidated Laboratory Services (DCLS) for the Ambient Water Quality Monitoring (AWQM) Project. The associated responsibilities depicted in Figure 1 for the DEQ organization of the project are as following:

Regional Field Staff: Conduct all office and field related duties directly affecting sample collection and handling.

Regional Environmental Specialist Senior: Responsible for Electronic Data Transfer (EDT) system related affairs in the regions. In the event of EDT failure, ensure timely transfer of information to DCLS via EDT or alternate measures. Manages day to day operation of Ambient Project in the region. Supervises regional conductance of the project in accordance with this quality assurance project plan. Coordinates routine ambient project activities. Provides input and implements Regional Technical Services Supervisor recommendations regarding program development, implementation and overall program management.

Regional Technical Services Supervisor: Makes recommendations for corrective action requested by regional personnel. Assures that activities in the regions meet requirements of the program of this project plan. Provide recommendations regarding the development, implementation and overall management of the program.

Laboratory Liaison: Coordinates program activities between the regional office staff and DCLS including scheduling sample collection based on laboratory capabilities. Manages the sample status report. Reviews data flagged by automated data validation program. Manages all program EDT operations. Verifies program's data storage.

Quality Assurance Officer: Revising and updating existing Quality Assurance Program Plan, Quality Assurance Project Plan and Agency Standard Operating Procedures Manual to ensure that approved practices and procedures are available for use by project personnel. Coordinates QA activities among state federal and laboratories to ensure sample quality and laboratory data validity, monitors laboratory performance through the use of a blind check sample program and performs inspections and recommends corrective action, when necessary. Presents training in the field sampling and measurements; conducts/ coordinates agency audits of the program; reports to management on the quality assurance

aspects of the program and where appropriate, make recommendations for corrective action.

Monitoring Coordinator: Implementation of the Water Quality Monitoring Plan and managing the Commonwealth's water quality monitoring strategy through the formal establishment of program policy, objectives, priorities and methodologies. Participates in specialized intensive scientific studies in water quality, seeking improved technologies and methodologies in the detection and quantification of environmental pollutants.

Ambient Water Quality Monitoring Program Planner: Responsible for overall strategy and functioning of the monitoring program. Assisted in duties by supporting staff including QA Officer and Water Quality Monitoring Coordinator and by cooperation from planning mangers and Technical Services Supervisors at regional offices throughout the state.

Environmental Technical Services Administrator: Assures that activities in the regions meet requirements of the program and this project plan. Provide recommendations regarding the development, implementation and overall management of the program.

Senior Programmer: Manages, monitors and maintains the related computer programs including the EDT system and data validation program.

Programmer/ Analyst: Runs computer programs including data validation and EDT data Transfer.

A.5 PROJECT/TASK DESCRIPTION

The ultimate goal of the Ambient Water Quality Monitoring Program is provide accurate data that will permit the evaluation, restoration and maintenance of the quality of the Commonwealth's waters at a level consistent with such multiple uses as prescribed by Federal and State laws. When physically and economically feasible, this goal is extended to include the restoration of the State's water to the pristine quality enjoyed by our forefathers, in an effort to guarantee the continued quality of our waters so that future generations may enjoy the same benefits. Specific elements of this goal include the prevention or reduction of pollution and other stressors in aquatic systems in order to conserve and improve ambient water quality conditions, maintain the natural biological integrity of ecosystems and promote public health. Although the importance of the Commonwealth's continued economic growth can not be denied, in evaluating the maximum benefit

for the greatest number we must consider the wellbeing of future generations as well as preservation of our native fauna and flora.

The overall goal is approached, in part, by means of a network of over 1000 active surface water monitoring sites administrated directly by the Ambient Water Quality Program. These permanent, semi-permanent and temporary stations are distributed from the small Atlantic Coastal Plain streams of Virginia's eastern peninsula to the mountainous southwestern extremity of the state. The extensive system of sampling sites unites the six areas of regional responsibility within the Commonwealth of Virginia into a single, integrated network of water quality monitoring stations, with overall objective of providing the best possible information on ambient water quality while maximizing the geographic coverage available.

The Ambient Water Quality Monitoring Program consists of a statewide network of stations used to generate water quality data. The program provides data for periodic assessment and review of state waters as required by section 305(b) of the Clean Water Act. It is also provides information on the quality of these waters for use in agency water quality planing and management activities, and for use by public and private groups as well as local, state and federal organization.

Data generated by the AWQM program is used primarily in the 305(b) report submitted to USEPA. This biennial report is the state's primarily water assessment and directs continuous planning and implementation activities in accordance with the agency's strategic management plan. Data extracted from STORET X are analyzed by in-house computer program for comparison with Virginia water quality standards.

The data from the program are used in modeling for Virginia Pollution Discharge Elimination System (VPDES) effluent limits, prioritizing construction grant proposals and other water quality management decision. The data are also provided to the public, consultants, environmental organizations, local governments, other state agencies, and federal agencies such as USEPA and U.S. Geological Survey. These groups to evaluate water quality conditions throughout the state use the data. USEPA also uses the information to assess national trends and identify any emerging problems.

Figure 1 DEQ ORGANIZATION FOR AWQM NETWORK

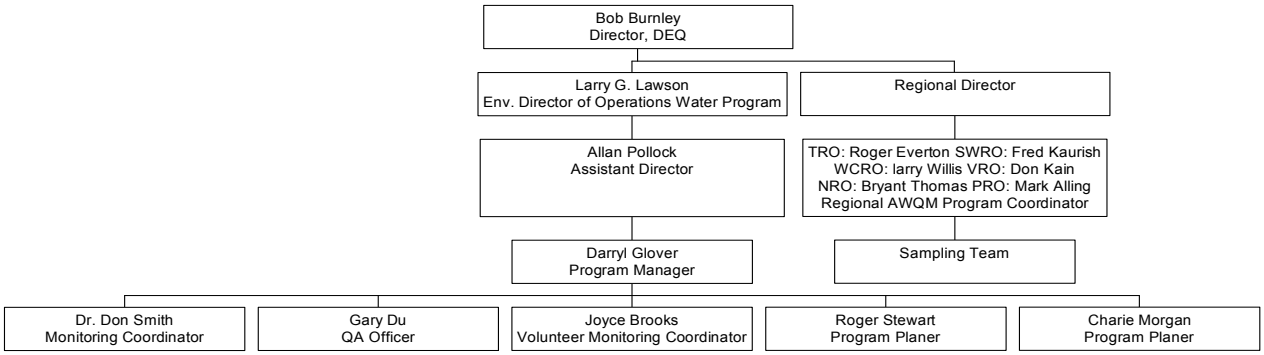
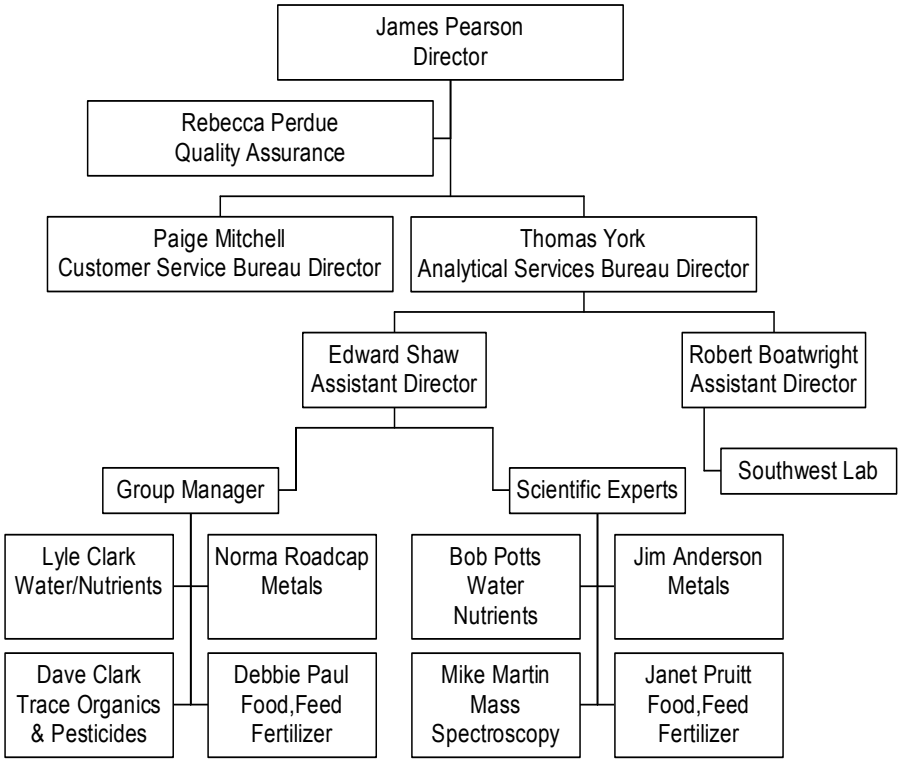


Figure 2 DCLS ORGANIZATION FOR AWQM PROGRAM



A6. QUALITY OBJECTIVES AND CRITERIA FOR MEASUREMENT DATA

Data Quality Objectives

Data Quality Objectives are qualitative and quantitative statements that specify the quality of data required to support specific WQA decisions. DQOs also specify the level of the uncertainty that a decision maker is willing to accept in results derived from monitoring data, when the results are used in a regulatory or programmatic decision, such as establishing analytical method requirements, establishing sampling protocols and revision or development of industry standards.

The DQOs defined in this section were developed by the WQA using existing performance information on the methods and procedures contained in this document. Because DQOs are established through an iterative process, these values may be adjusted by the WQA QA officer as a result of evaluations of performance data generated during this program.

The main objective of this document is to provide monitoring data of known and consistent quality to the WQA. These data will be used in characterization the waterbody, identifying long-term trends, and providing data and guidance to managers and modelers during the restoration phase.

The levels of quality of sampling activities are expressed in terms of comparability, representativeness, precision, accuracy, and completeness using the following criteria.

- Following the sampling procedures and sample locations recommended in this document may ensure sampling comparability and representativeness of data generated to meet the WQA needs.

- Overall precision (sampling and analytical) is assessed through field replicate measurements/analyses, and is express as coefficient of variation (CV). Sampling precision can be evaluated can be evaluated by comparing overall precision to measurement/analytical precision.

- Overall accuracy is assessed through field spike analyses, and is express as percent recovery. Sampling accuracy can be evaluated by comparing overall accuracy to measurement/analytical accuracy. However, these are not recommended.

- Sampling completeness is calculated based on the ratio of samples collected to samples that were planned, and is expressed as percent completeness.

The level of quality of measurement and analytical data are expressed in term of comparability, represnetiveness, precision, accuracy, completeness, and method detection limits (MDL) using the following criteria.

- Measurement/analytical comparability and representiveness of data generated will be ensured through adherence to the measurement and analytical procedures described methods document.

- Precision expressed as coefficient of variation (CV) for measurement and analytical data is calculated based on replicate measurement/analyses. The precision for water quality analyses is provided in Table 1.

- Accuracy expressed as percent of reference of value, of measurement data is calculated based on measurements of standard reference materials (where available) and calibrating reference techniques.

- Accuracy expressed as percent recovery of analytical data is calculated based on the analysis of spiked samples and reference materials. The accuracy for water quality analyses is provided in Table 1.

- Completeness of measurement data is calculated based on the ration of measurements made to measurements planned, and is express as percent completeness.

- Completeness of analytical data is calculated based on the ratio of samples that are analyzed to the number of samples collected, and expressed as percent completeness. The completeness for water quality analyses is provided in Table 1.

The method detection limit (MDL) should be determined for all parameters using the procedures in the Federal Register, 40 CFR Part 136 Appendix B (Revision 1.11). The MDL are provided in Table 2.

Table 1 Objectives for Water Quality Analyses

Parameter	Precision	Accuracy	Completeness
Ammonia	<20%	10%	95%
Toatl Phosphorus	<20%	10%	95%
TKN	<20%	10%	95%
Nitrate	<20%	10%	95%
Nitrite	<20%	10%	95%
Orthophosphate	<20%	10%	95%
TSS,FSS,VSS,TDS, TS,FS,VS	<20%	-----	95%
Alkalinity	<20%	-----	95%
Chloride	<20%	10%	95%
Sulfate	<20%	10%	95%
BOD	<20%	10%	95%
TOC	<20%	10%	95%
Chlorophyll	<20%	10%	95%
Metals	<20%	30%	95%
Pesticides, Herbicides	<30%	30%	95%

Table 2 Method Detection Limits

Water/Nutrient

Parameter	mg/L	Parameter	mg/L
Ammonia	0.04	Nitrate	0.04
Nitrite	0.01	Orthophosphate	0.01
TKN	0.1	Total Phosphorus	0.01
Alkalinity	1.0	BOD	1.0
COD	5.0	Hardness	1.0
Chloride	0.1	Conductivity	0.05
Sulfate	0.1	Tannin/Lignin	0.01
TOC	1.0		

Metals

Parameter	Aqueous(μg/L)	Sediment(mg/kg)
Aluminum	0.064	
Antimony	0.064	
Arsenic	0.041	
Cadmium	0.074	
Calcium	23.8	
Chromium	0.069	
Copper	0.040	
Iron	2.60	
Lead	0.033	
Magnesium	2.6	
Manganese	0.06	
Mercury	0.05	
Nickel	0.087	
Selenium	0.047	
Silver	0.071	
Thallium	0.02	
Zinc	0.141	

Pesticides & Herbicides

Parameter	Water Samples (µg/L)	Sediment Samples(ng/g)
Aldrin	0.01	5
Alpha-BHC	0.01	5
Beta-BHC	0.01	5
Delta-BHC	0.01	5
Gamma-BHC	0.01	5
Chlordane	0.1	10
4,4'-DDD	0.01	15
4,4'-DDE	0.01	5
4,4'-DDT	0.01	10
Dieldrin	0.01	10
Endosulfan I	0.01	10
Endosulfan II	0.01	10
Endosulfan sulfate	0.01	10
Endrin	0.05	25
Endrin aldehyde	0.01	20
Heptachlor	0.01	5
Heptachlor epoxide	0.01	5
Toxaphene	0.5	
PCB-1016	0.5	5
PCB-1221	0.5	5
PCB-1232	0.5	5
PCB-1242	0.5	5
PCB-1248	0.5	5
PCB-1254	0.5	5
PCB-1260	0.5	5
2,4'-5-T	0.1	
2,4'-D	0.3	
2,4'-DB	0.3	
Alachlor	0.01	
Atrazine	0.1	
Dicamba	0.1	
Dichlorprop	0.3	
Guthion	0.5	
Kepone	1.0	
Malathion	0.1	
Mirex	0.5	10
Pentachlorophenol	0.1	
Silvex	0.1	

A.7 SPECIAL TRAINING REQUIREMENTS/CERTIFICATION LISTED

Each field team member must be experienced or have received proper training on this project's requirements for sampling, sample handing and custody, and field documentation.

Each field team member received properly training to comply with all applicable Occupational Safety and Health Administration requirements.

A.8 DOCUMENTATION AND RECORDS

A.8.1 Field Documentation

Each field sampling sheet and tags must be completed either in the office or on-site at the time sampling occurs. Field staff record program code, station ID, date and time collected, survey depth, collector, catalog number, group code, container #, unit code information on the field data sheet. The field data sheet should be sent to the laboratory. The summary of analytical turn-around time is provided in table 3.

Table 3 Summary of Analytical Turn-Around Times (TAT)

Group Code	Standard TAT (Days)
NUT3P	7
NUT4	7
NME1	11
NME2	11
NME4	11
NME5	11
NME7	11
NME9	11
NME11	11
NME13	11
FCLR	7
FCMP	3
FCMPN	7
MET1S	14
PES1S	14
CMETA	30
PART	11
SOLID	11
TOC	11

A.8.2 Document Control

The goal of the document control program is to ensure that all documents and electronically stored information from a specified cruise are accountable, secure, and completely retrievable. Document control is recommended for each activity to include electronic as well as hardcopy documentation. Accountable documents should be include but not limited to field and laboratory logbooks, sample work sheets, bench sheets, and other documents relating to the sample or sample analyses.

A.8.2.1 Logbooks

Logbook entries should be dated (month/day/year) and signed by the person responsible for performing the activity at the time an activity is performed.

Logbook entries should be in chronological order.

Pages in both bounded and unbounded logbooks should be sequentially numbered.

Corrections to supporting documents and raw data should be made by drawing a single line through the error and enter the correct information. Corrections and additions to supporting documents and raw data should be initialed. All notions should be recorded in ink.

A.8.2.2 Consistency of Documentation

A field specialist senior responsible for the organization and assembly of the data package should be assigned.

All copies of field and laboratory documents should be complete and legible.

The field specialist senior assemble and cross-check the information on sample tags, laboratory sheets, personnel and instrument logs, and other relevant data ensure that data pertaining to each particular sample or sample delivery group is consistent throughout the data package.

A.8.2.3 Storage of files

Field and laboratory documents will be maintained in a secure location for a period of seven years from the date of sample delivery.

B.1 SAMPLING PROCESS DESIGN

The Ambient Monitoring Program emphasized sampling from major rivers and streams, in the effort to characterize the water quality of relatively extensive hydrological basins. As the increasing number and complexity of factors influencing water quality became more apparent, emphasis shifted to the characterization. When necessary, the application of local remedial measures to impairments in smaller tributary streams that contributed individual, and often different, factors that influenced water quality. Currently, The Ambient Water Quality Program concentrates on smaller hydrological units, local watersheds and homogeneous stream segments to characterize water quality and identify the factor responsible for its local variations. Such stream segments are delimited not only by the physical and chemical characteristics of their water column and substrates, and the associated biological communities, but also by the geological, topographic, and land use characteristics of the region. As matter of policy, the overall length of such homogeneous segments is limited to a maximum of approximately 25 miles in major rivers and 10 miles or less in smaller streams. In longer homogeneous stream extensions the ability of the stream itself to absorb pollutants, thus modifying its own water quality, may mask significant sources of more localized environmental impairments.

The monitoring network consists of more than 600 stations for which over 5000 water column and sediment samples are collected each year. Monitoring stations are sampled monthly, bimonthly, quarterly, or annually for select physical and chemical parameters. In addition to field measurements, the Division of Consolidated Laboratory Services performs approximately 90000 analyses on these samples annually. The AWQM program is all year around continuous work schedule. All stations are sampled for the parameters as listed in Table 3.

B2. Sampling Methods Requirements

Standard Operating Procedures are contained in the DEQ Water Quality Assessment Operating Procedure (WQAOP) manual and address specific program requirements for:

- Field sample collection procedure and methods
- Field analyses
- Equipment
- Process for preparation and decontamination of sampling equipment
- Preventive maintenance
- Sample identification
- Preparation of sample containers

To ensure sample integrity for this program, requirements have been established for sample collection, container, and preservation. These requirements for water column and

sediment samples are summarized in Table 4. This table provides information on the sample containers, sample volumes, preservation, and maximum holding times.

B.2.1 Field Quality Control Samples

The following field QC samples will be collected to assess laboratory and field precision and laboratory accuracy.

B.2.1.1 Filed Replicate Samples

Field replicate samples will be collected and analyzed to evaluate sampling precision. A field replicate is a sample taken at the same location and depth as a sample. The replicate and sample should be taken in quick succession of each other. One of the bottle sets will be labeled as primary sample and one will be submitted to the laboratory blind with a fictitious sample identification number. The blind field will be analyzed in the same manner as the primary samples. A field replicate should be collected once every 20 samples. The relative percent difference should not exceed 20%.

B.2.1.2 Preservative Reagents Blank

In order to ensure a preservative is contaminate free, it must be tested before it is used for sample preservation. Summit preservative reagents blank prior to the use of a new lot of preservative. The field reagents blank should not exceed 1/10 of practical quantification limits.

B.2.1.3 Equipment Blank

To ensure the sampling device has been effectively cleaned, fill the device with deionized water or pump deionized water through the device, transfer to sample bottles, preserve, and return to the laboratory for analysis. The field equipment blank should be processed at beginning sampling day. This may be performed in the regional office prior to going to field. One equipment blank sample will be collected per month per person. The equipment blank should not exceed practical quantification limits.

B.2.1.4 Performance Evaluation Samples

Every year a total of four double-blind water matrix PE samples will be submitted to the analytical laboratory to evaluate analytical accuracy. The PE samples will be submitted once every quarterly. The PE samples will contain known concentration of analytes. The laboratory results will be evaluated against the certificates of analyses by the DEQ QA

Officer to ensure that laboratory maintains good performance. Double blind PE samples will be obtained from a commercial vendor. The PE samples will be shipped from the field or regional office lab to the analytical laboratory in the containers identical to those used for the field samples.

Table 4 Sample Container & Preservation Requirements for Water Matrices

Parameters	Containers	Volume Required	Preservation	Holding Time
Non Metals				
Alkalinity	Gallon Plastic Cubitainer	3 Liter	Cool to 4^0C	14Days
Chloride, Sulfate				28Days
Conductivity				
TSS,FSS,VSS				7Days
TDS,TS,FS,VS				
Turbidity, BOD				48 Hours
Hardness	250ml Plastic Bottle	250ml	H_2SO_4 to pH<2,Cool to 4^0C	6 Mos.
TOC				28Days
Nutrients	250ml Plastic Bottle	250ml	H_2SO_4 to pH<2,Cool to 4^0C	28Days
Total Phosphorus Total Kjedahl Nitrogen				
Nitrate Nitrite Orthophosphate Ammonia	250ml Plastic Bottle	250ml	Cool to 4^0C	48Hours
Fecal Coliform	Sterilized 100ml Plastic Bottle	100ml	Cool to 4^0C	24Hours
Metals	Precleaned Plastic 1L Bottle	1L	HNO_3 to pH<2,Cool to 4^0C	6Mos. Except Mercury 28 days
Pesticides, Herbicides	Amber 1L Glass Bottle	2X1L	Cool to 4^0C	7 Days Extraction,14 Days Analysis
Chlorophyll			Cool to 4^0C	Field filtered

				extracted in 3 weeks
Sediment				
Metals	32 Oz. Plastic or Glass Wide Mouth Jar	10Grams	Cool to 4^0C	6Mos. Except Mercury 28 days
Pesticides	32 Oz.Glass Wide Mouth Jar	10Grams	Cool to 4^0C	Not Determined

B3 SAMPLE HANDLING AND CUSTODY REQUIREMENTS

Samples will be shipped via courier service to DCLS next day. It is important that coolers are packed sufficient ice to chill the samples to 4^0C.Once transferred to the refrigerator at analytical laboratory, the samples will be stored and maintained at 4^0C. Standardized procedures are described in the WQAOP manual.

Sample custody procedures are an integral part of the laboratory and field operations. Since the ambient monitoring data are not used for legal purposes formal chain of custody procedures are not required. Sample custody procedures are contained in the WQAOP manual and ensure the integrity of the samples received by DCLS. These field sampling operations include:

- Procedures for filling out sample label tags
- Documentation of specific sample preservation method
- Documentation of sample custody in the field

DCLS will have responsibility for sample custody upon receipt of samples by central receiving. These procedures are described in detail in the individual DCLS section's QA plan.

B4 ANALYTICAL METHODS REQUIREMENTS

The analytical methods selected for AWQM program are described in table 5. All these methods are standard methods which either EPA or standard approved methods. The required equipment and reagents are included in each individual laboratory technical procedure manual.

Actions for problem resolutions will be implemented. These actions shall be aimed at eliminating the problem whenever possible. It is encouraged that action be taken at the lowest level to resolve problem. Corrective actions will be reported through management and documented for quality assessment where additional actions may be taken.

Groups will report monthly to the QA Committee the following information; monitoring data, identified problems, problem assessment, corrective actions initiated to improve services, follow up plans and outcomes. Committee members may provide suggestions and recommendations. Each identified problem will be given a control number and the outcome of actions taken tracked by the QA committee. A problem file will not be closed by the committee until follow up plans have been completed and a successful outcome achieved.

Table 5 Parameters, matrices and Analytical Methods for AWQM Stations

Parameters	Water Samples	Sediment Samples	Analytical Method
Field			
PH	X		
Conductivity	X		
Dissolved Oxygen	X		
Temperature	X		
Laboratory			
Alkalinity	X		STD MTDS 2320B
Hardness	X		EPA 130.1
Ammonia	X		EPA 350.1
TKN	X		EPA 351.2
Nitrate plus Nitrite	X		EPA 353.2
Nitrite	X		EPA 353.2
Total Phosphorus	X		EPA 365.4
Orthophosphate	X		EPA 365.1
BOD	X		STD MTDS 5210B
COD	X		STD MTDS 5520 D
TOC	X		STD MTDS 5310B
FCMF	X		STD MTDS 9222 D
Total Solids	X		STD MTDS 2540B
Volatile Solids	X		STD MTDS 2540 E
Fixed Solids	X		STD MTDS 2540 E
Total Suspended Solids	X		STD MTDS 2540D
Volatile Suspended Solids	X		STD MTDS 2540 B
Fixed Suspended Solids	X		STD MTDS 2540 B
Total Dissolved Solids	X		STD MTDS 2540 C
Chloride	X		STD MTDS 4500-CL C

Sulfate	X		EPA 375.4
PH	X		STD MTDS 4500-H+ B
Conductivity	X		STD MTDS 2510B
Turbidity	X		STD MTDS 2130 B
Chlorophyll a	X		EPA 455.0
FCMPN	X		STD MTDS 9221 C
Color-PCU	X		STD MTDS 2120 B
Tannin/Lignin	X		STD MTDS 5550 B
Pesticides	X		EPA 608
Aluminum	X	X	Water Samples :
Antimony	X	X	EPA 1638
Arsenic	X	X	Sediment Samples:
Cadmium	X	X	Pretreatment
Calcium	X	X	SW846-3051
Chromium	X	X	Analyses:
Copper	X	X	EPA 200.8
Iron	X	X	
Lead	X	X	
Magnesium	X	X	
Manganese	X	X	
Mercury	X	X	
Nickel	X	X	
Selenium	X	X	
Silver	X	X	
Thallium	X	X	
Zinc	X	X	
Pesticides		X	

B5 Quality Control Requirements

Quality control is an integral part of determining the quality of both field and laboratory data quality control samples generated by field and laboratory procedures are used to assess data quality.

Five percent of the samples submitted to DCLS will be field quality control samples (field replicates). Field equipment blank should be collected one per month per person. The quality control samples will be prepared and analyzed for all parameters of interest and for each sample matrix.

B.5.1 Quality Control Acceptance Criteria for Measurement Data

DCLS laboratories assess internal quality control by including ten or twenty percent of all samples analyzed as laboratory quality control samples. The QC limits set as project acceptance limits for measurement data are listed in Table 6. These criteria will be used in data validation to assess whether the program's QA objectives have been met.

B.5.1.1 Precision

Precision measures the reproducibility of repetitive measurements. It is strictly defined as the degree of mutual agreement among indepentendent measurements as the result of repeated application of the sample process under similar conditions. Precision acceptance limits for the QC analyses discussed below are shown in the Table 6.

Analytical precision is a measure of the variability associated with duplicate or replicate analyses of the same sample in the laboratory and is evaluated by analysis of laboratory QC samples, such as MSD. If the recoveries of analytes in the specified control samples are comparable within established control limits, then precision is with limits.

Total precision is a measure of the variability associated with entire sampling and analytical process. It is evaluated by analysis of duplicate or replicate field samples and measures variability introduced by both the laboratories and field operations. Field replicate samples are analyzed to assess field and analytical precision. One field replicate will be collected for every 20 samples.

Replicate results will be assessed using the relative percent difference (RPD) between replicate measurements. RPD limits for laboratories are stated in the table 6. The RPD will be calculated as follows:

$$RPD=(200)\ (X_1 - X_2)\ /(X_1 + X_2)$$

Where X_1 is the larger of the two observed values and X_2 is the smaller of the two observed values.

B.5.1.2 Accuracy

Accuracy is a statistical measure of correctness and includes components of random error and systematic error. It reflects the total error associated with a measurement. A measurement is accurate when the value reported does not differ from the true value or known concentration of the spike or standard. Accuracy acceptance limits for the QC analyses discussed below are given in Table 6.

Accuracy of laboratory analyses will be assessed by initial and continuing calibrations of instruments and analysis of blanks, laboratory control samples matrix spike and blind PE

samples. Laboratory accuracy is expressed as the percent recovery (%R). Percent recovery will be calculated as follows:

$$\%R = (100)\ (X_S - X) / T$$

Where X_S is the measured value of the spiked sample, X is the measured value of the unspiked sample, and T is the true value of the spike solution added.

Field accuracy often is assessed through the analysis of field equipment blanks. Analysis of blanks monitors errors associated with the sampling process when sampling equipment is decontaminated between samples and reused.

B.5.1.3 Representativeness

Representaiveness is the degree to which data accurately and precisely represent a characteristic of a population, parameter variations at a sampling point, a process condition, or an environmental condition. Experimental design, statistical sampling techniques, and sample collection, preservation and handling are interactive factors that directly affect achievement of field sample representativeness. The experimental design for the AWQM program is described in detail in the project description. SOP detailed in the WQAOP manual are used by the field personnel that address sample collection, preservation and handling to maintain minimum standards of representativeness in the field. Although these SOPs detail specific operations for the field sampling and handling, the SOPs also provide a mechanism, which gives allowance for the judgement of field personnel. If abnormal circumstances do occur relative to the sampling and/or site selection, the field personnel may document this and take the appropriate action. The corrective action plan for AWQM program also provides a mechanism to identify and correct procedures, which affect the representiveness of the data.

B.5.1.4 Comparability

Comparability is an expression of the confidence with which one data set can be compared to another. Comparability of ambient data is the summation of a quality product at each phase of the data gathering process. It includes uniform sampling and analytical methods for field and laboratory procedures, representative sampling and sample handling procedures and procedures for reduction, validation, and reporting of laboratory and environmental data. Essential to data comparability is not only the attainment of desired data quality but also establishing and documentation the quality achieved.

In the sampling phase, the staff can use field blanks, field replicates, and SOPs incorporating reliable QA procedures to ensure a high quality product. These techniques combined with requirements for containers, sampling preservation, and holding times

will yield a reasonable assurance of achieving the required confidence levels in the sampling phase.

Methods of analysis are standardized for the AWQM program. The analytical methods requirements section includes the analytical method used by DCLS by each parameter. Quality control samples along with appropriate statistical techniques are used to ensure accuracy and precision in the production of laboratory data. The sampling phase conducted by DEQ and the data generated by DCLS maintain a level of confidence allowing valid comparison both within the AWQM program and between similar environmental data sets.

B.5.1.5 Completeness

Completeness is the amount of valid data obtained compared to the amount that was planed. The number of valid results divided by the number of planned results, expressed as a percentage, determines the completeness of the data set. Completeness is calculated as follows:

% Completeness = (100) (number of valid results / Number of planned results)

Estimates of completeness for the monitoring parameters for the ambient program will exceed 95%. Factors that occasionally invalidate samples include sample preservation, holding time, samples ID, sample storage, insufficient sample volumes, and container loss and breakage.

Table 6 QC Sample Analyses and Acceptance Criteria for Water/Nutrient Lab

Description and use	Frequency of Application	Acceptance Criteria	Laboratory Corrective Action
Instrument Calibration	Each analytical run	Correlation coefficient ≥ 0.995	Repeat calibration
Method blank	One per sample run per matrix	Not exceed 1/10 of the PQL	Stop analysis and trouble shooting
Initial Calibration Verification	At the beginning of run	± 10% of actual value	Stop analysis, make correction
QC sample	At the beginning and end run	Recovery between ± 3 SD of the true value	Stop analysis recalibrate instrument
Continue Calibration Verification	One per 10 sample	± 10% of true value	Samples following an out of control CCV are rerun until the system is back in control per an acceptable CCV
Matrix Spike	One per 10 samples	Recovery between 90% and 110%	Rerun sample. If still out of control, qualify the data in the report.
Matrix Spike Duplicate or Sample Duplicate	One of 10 samples	Relative percent difference ≤ 10%	Rerun sample. Report out of control samples to user agency

Table 7 QC sample Analyses and Acceptance Criteria for Metal Lab

Description	Frequency of Application	Acceptance Criteria	Laboratory Corrective Action
Instrument Calibration	Each analytical run	Correlation coefficient ≥ 0.995	Repeat calibration
Blanks	At the beginning and end of sample run and every tenth sample	Not exceed 2.2 MDL	Repeat with last 10 samples
Curve Verification Standards	At the beginning and end of sample run and every tenth sample	±10% of actual value	Recalibration must be done to continue the run
Matrix Spikes	10% of samples	±30% of spiked value	Repeat
Matrix Spikes Duplicate	One per 20 samples	±20% relative percent difference	Repeat
Quality Control Sample	Once per analytical run	±10% of true value	Repeat
Laboratory Control Sample	One per 20 digested sample	±15% of actual value	Repeat
Sediment Laboratory Control sample	One per 20 digested sample	Mean ± 2 standard deviation	Repeat

B6 Instrument/Equipment Testing, Inspection, and Maintenance Requirements

The field specialist inspected field instruments and equipment in the lab daily. Corrective action is immediately taken when the problems were found. Backup instruments /equipment are used when available. In the case that backup instrument or equipment is not available, the analysis of that parameter is not taken.

Preventive maintenance is that maintenance procedures scheduled to be performed at specific time intervals to ensure proper instrument performance. Analytical and field instruments and ancillary equipment must be maintained in good operating condition to minimize major repairs and down time.

Laboratory instruments SOP's include preventive maintenance procedures as well as performance checks and calibration procedures. These procedures are performed on a defined schedule or where appropriate, base on the results of performance checks or after a specified number of hours of operation. Specific procedures for laboratory instruments are included in the individual DCLS laboratory technical procedure manuals.

For the AWQM program, preventive maintenance schedules have been established for all field testing equipment. If performance checks or calibration procedures indicate a problem, appropriate maintenance is conducted immediately or the equipment is returned to the manufacturer for service. Defective equipment will not be used operationally until repaired and satisfactory performance results are achieved.

Each regional office has responsibility for ensuring that the preventive maintenance schedule listed in the WQAOP Manual is followed. A preventive maintenance logbook is maintained in the regions documenting maintenance performed on each instrument. The regional program coordinator periodically to identify equipment, which has a high repair record and to determine which specific items require more frequent repairs reviews this logbook. Depending on the difficulty of replacement of these items they may be added to the list of critical spare parts to be maintained at the regional office.

SOPs for field equipment preventive maintenance and documentation in logbooks are contained in the WQAOP manual. The manual also contains a list of critical spare parts, which should be available at the regional offices.

B7 Instrument Calibration and Frequency

B.7.1 Field Equipment

A calibration logbook is maintained for each piece of field equipment at each region. Each book contains a set of instructions on how the calibration should be performed and a chart listing the date, time, the pH standard used, precalibration, postcalibration, Saturated dissolved oxygen, temperature, barometric pressure reading, conductivity calibration reading, initials of personnel, and comments. Manufacturers recommended methods must calibrate all probes. The following is information of the field equipment, the calibration required, and the frequency.

Conductivity sensor: The conductivity probe must be calibrated against a reference solution, according to manufacturer's specifications. As a minimum conductivity standard should be verified before and after each run.

PH probe: As a minimum the pH probe must be calibrated at the beginning and end of every sampling day against two standard buffer solutions that bracket the expected pH of the samples to be measured (e.g. 4&7 0r 7&10). The pH probe must be rinsed with deionized water and soaked in deionized water when not in used. If the probe drifts ±0.2 pH units at the end of day, the validity of the readings should be verified.

Dissolved Oxygen probe: The dissolved oxygen probe must be calibrated using air-saturated water at beginning and end of each sampling day. If the probe drifts ±0.3 mg/l at the end of day, the validity of the readings should be verified. Periodic verification checks should be performed using Winkler titration.

Thermometer: Calibrate the thermometer once a year against a NIST certified thermometer over a range of temperature.

Pressure sensor: Calibrate the depth sensor once a year according to the manufacturer's instructions.

B.7.2 Laboratory Equipment:

Laboratory equipment calibration procedures are included in the individual laboratory technical procedure manuals.

B8 Inspection / Acceptance Requirements for Supplies and Consumables

The field specialist senior inspects chemicals, regents, bottles, and cubic containers upon arrival. Any broken bottles and containers are shipped back to the manufacturer for replacement.

The laboratory technical staff will be responsible for inspecting incoming equipment and supplies before placing them in service. The manufacturer's specifications for product performance and purity will be used as criteria for acceptance or rejection of supplies and consumables.

B10 Data Management

B.10.1 Data Recording

Data for this project will be collected by handwritten entries. Field observations and records such as sample collection information will be primarily recorded manually using the form.

B.10.2 Data Quality Assurance Checks

QA checks of data as early as possible are essential to provide early warning of potential problems. The DEQ staff routinely performs range check. Range checks are run at DEQ's mainframe computer. Perform automatic range checks of field and laboratory results for valid entry, such that only numbers that are possible for that parameter are accepted.

B.10.3 Data Reporting, Transmittal, Storage and Retrieval

The scheduled samples are assigned a laboratory number. The field information is transmitted through EDT system to a PC computer in laboratory central receiving. In the event of field information transmittal failure, laboratory sheets are used to provide the information to DCLS. Receiving personnel check samples delivered against samples scheduled. Central receiving correlated samples received with laboratory numbers, logs in the samples, generates worksheets and distributes the samples and work sheets to the laboratories for analysis. Weekly status report sheets generated by DCLS keep the DEQ abreast of the status of recently received samples. After analysis, the data are reduced to appropriated units and reviewed, approved by the individual laboratories before being transmitted to central receiving for entry into the laboratory data system. Data are then

transmitted to the DCLS PC computer and finally to the DEQ mainframe. The data go through a series of screens and reviews to identify invalid, qualified or QA supported data. The qualified and QA supported data are transmitted into the EPA's STORET X system for access to users. All the hard-copy originals of field forms and laboratory sheet will be bound and stored at a secure facility for a minimum of seven years following delivery of the report.

B.10.4 Data analysis

WQA staff at central office will perform data analysis for AWQM. The appropriate statistical methods will be used to analyze data.

C1 Assessments and Response Actions

C.1.1 Audits of Data Quality

Field blank and field duplicate data will be reviewed in order to assess the quality of sampling activities.

Analytical and measurement data should be reviewed in order to assess the quality of measurement and analytical activities, respectively.

Metadata should be reviewed in order to assess precision and accuracy.

The Quality Assurance Officer has the ultimate responsibility to accept or reject data.

C.1.2 Technical Systems Audits

C.1.2.1 Field Sampling Audits

Field sampling audits evaluate field operations with SOPs and other requirements established in the project plan and WQAOP manual. Field sampling audits will be conducted at least twice a year. Additional audits will be scheduled if warranted by audit observations and findings. The primary audit elements for the ambient program are:

- Availability, appropriateness and use of field SOPs.
- Sampling methodology
- Sample handling procedures
- QA procedures

- Field instrument operation logbook
- Field maintenance logbooks
- Field documentation
- EDT information transmittal
- Field data quality, quantity and timeliness
- Follow-up on previous corrective action and recommendations

The Quality Assurance Officer conducts the audit at least once a year. The QA Officer will prepare the audit report which discuss deficiencies found during the on-site evaluation with recommendations for corrective action. The report will be forwarded to the regional Technical Service Supervisor.

C.1.2.2 Laboratory audits

Internal and external lab audits are conducted by DCLS to monitor the overall effectiveness of the quality assurance system. The Quality Assurance Plan for DCLS describes external systems audit procedures used by the Bureau of Chemistry. The systems audits are conducted by an audit team composed of a Bureau of Chemistry QA team member, a lab section representative, and a member of the QA and lab inspection section. The systems audits are conducted at least annually and include evaluation of laboratory:

- Sample storage and holding time
- Sample tracking
- Sample preparation and analytical procedures
- Quality control procedures and QC data evaluation
- Data reduction and reporting

Internal audits are conducted quarterly, usually by each unit technical supervisor, to examine the performance of the data generation activities of the laboratories. The specific makes up of the audit team and the procedures to conduct laboratory audits are contained in each section's quality assurance plan. Internal audits may include:

- Worksheet reviews for sample handling, analysis, standard integrity, instrument performance, calculations, sample reporting and QC chart.
- Review of performance on inter- and intralaboratory blind and check samples.
- Independent analysis of a sample

External laboratory systems and performance audits are conducted periodically by the DEQ and USEPA. DEQ QA officer is responsible for external audits of each laboratory. Split samples provide additional quality performance information. The laboratories participate annually in EPA performance valuation studies. EPA also conducts a biannual inspection of the laboratories. DCLS also perform self-audits of

the areas covered by the accrediting agencies during the "off inspection" year. DCLS provides a copy of EPA's audits and performance evaluations reports to the DEQ.

C.1.2.3 Performance Evaluation Samples

Performance evaluation (PE) samples are sent quarterly as double blind samples to the laboratory for water quality. Where available, commercial QC samples for nutrient and demand parameters, as well as solids are sent. The acceptance criteria will be the advisory limits are based on either plus/minus two times the standard deviation from estimated mean recovery. The advisory range represents the approximate 95 percent confidence interval. If performance evaluation samples results are failed outside the range, the corrective action will be taken.

C.1.3 Program Audits

This audit evaluates the AWQM program to determine whether the overall program has a sound technical basis and that data produced meets program objectives. The office of policy analysis conducts these audits and agency management identifies when these program audits will be conducted. Following the completion of the evaluation, a report with recommendations is prepared for agency management.

C.1.4 Corrective Action

The first level of responsibility for identifying the need for corrective action lies with field and laboratory technical staff during routine sampling and analysis activities. The second level of responsibility lies with any person observing deviations during field audits, while reviewing field documentation, or while reviewing laboratory results.

Each time the need for corrective action is identified, the problem will be documented on the corrective action request and tracking form. The form indicates the person responsible for identifying, implementing, and assessing the effectiveness of the corrective action.

C.1.4.1 Field Corrective Action

Corrective actions will be initiated if the field team is not adhering to the prescribed sampling or documentation procedures or if laboratory analyses are experiencing interference or systematic contamination due to field sampling procedures or sample handling protocol. Corrective actions begin with identifying the source of the

problem. Corrective action responses may include more intensive staff training, modification of field procedures, or removal of the source of systematic contamination. Once resolved, the corrective action procedure will be fully documented.

C.1.4.2 Laboratory Corrective Action

Problems should be resolved at lowest level possible. When monitored data exceed a threshold of acceptable limits corrective action should be taken immediately and all actions documented. Laboratory staff will notify supervisors when unsure of the appropriate corrective action. The QA committee member, senior chemists, principal, and manager will review corrective actions. The QA committee member will compile monitored data and corrective actions monthly and summit these data monthly to the QA committee. The QA committee will provide commendations and continue to monitor to ensure detected problems are resolved. If the initial corrective action fails to resolve the problem or a trend is established, the QA committee may make additional recommendations or establish an action team to seek a resolution. The goal of the laboratory is to detect problems early, implement changes to improve services, and monitor for effect.

C2 Reports to Management

In accordance with the agency Quality Management Plan, reports on the compliance status of the AWQM program will be summited to DEQ management on a quarterly basis.

Each quarterly report will address the following topic areas:

- Performance and system audits conducted.
- Evaluation of compliance with QA project plan.
- Evaluation of data quality measurement trend.
- Identification of problems, program needs and recommendations for solution.

QA officer will prepare these quarterly reports and copies will be sent to regional Technical Service Supervisors.

The Quality Management Plan also requires that the QA officer submit an annual status report summarizing all QA activities. The information identified in the AWQM program quarterly reports will be summarized and then included as part of the status report. The report will be summited the management identified previously.

D1 Data Review, Validation, and Verification

All AWQM field and laboratory data is reviewed by the DEQ QA officer to determine if the data meet Quality Assurance Project Plan objective. Decisions to reject or qualify data are made by the project manager and QA officer.

Standard laboratory methods used by DCLS include formulas for calculation of parameter values after the analysis of the samples. The laboratories have also established procedures for cross-checking calculations and checking for transmittal errors.

Data are validated through a series of quality control checks, screens, audits, qualifications, verifications and reviews. These procedures compare the generated data with established criteria to assure that the data are adequate for their intended uses. As field information and data are entered into EDT system, entry specific checks limit the possibility of transcription error. Reduced data generated by field and laboratory analyses are uploaded into the DEQ mainframe computer for validation. Data are examined by a series of four screens. EDT data entry, analytical, historical and quality control sample data screenings identify potentially comprised sample quality. Data are compared with acceptance limits for each screen for acceptance, rejection, or qualification. A review of field and laboratory documentation is conducted for data lying outside control limits established for the various QC screens. This review is used to determine if DEQ or DCLS staff noted any irregular condition during sample collection, handling, and analysis, which might have affected the data. Results from the QC screens and documentation review are used to accept, qualify or reject data for inclusion into the STORET X system. Figure 3 illustrates the flow for data validation prior to data entry into the STORET X system.

DCLS uses spikes, internal and external quality checks samples, replicates, and internal audits for each laboratory to ensure data validity. In addition, EPA conducts biannual performance evaluations and audits of laboratory performance. The DEQ summited double blind sample to the laboratory and use laboratory quality assurance audits to assess use of approved field and laboratory sample collection, handling, preservation and measurement procedures.

D2 Validation and Verification Methods

Data limits established for the EDT data entry, analytical, historical and QC sample screens are used to identify outliners and data falling within acceptable limits. Data falling within the criteria of one screen progress to the next screen. Field and laboratory documentation for data outside the control limits of a screen is reviewed.

D.2.1 EDT Data Entry Screen

Initial entry of sampling information and field data into the DEQ computer system must meet field specific criteria. Checks are made for valid identification of station, sampling run, parameters, collector, and field data within ranges accepted by STRORET X.

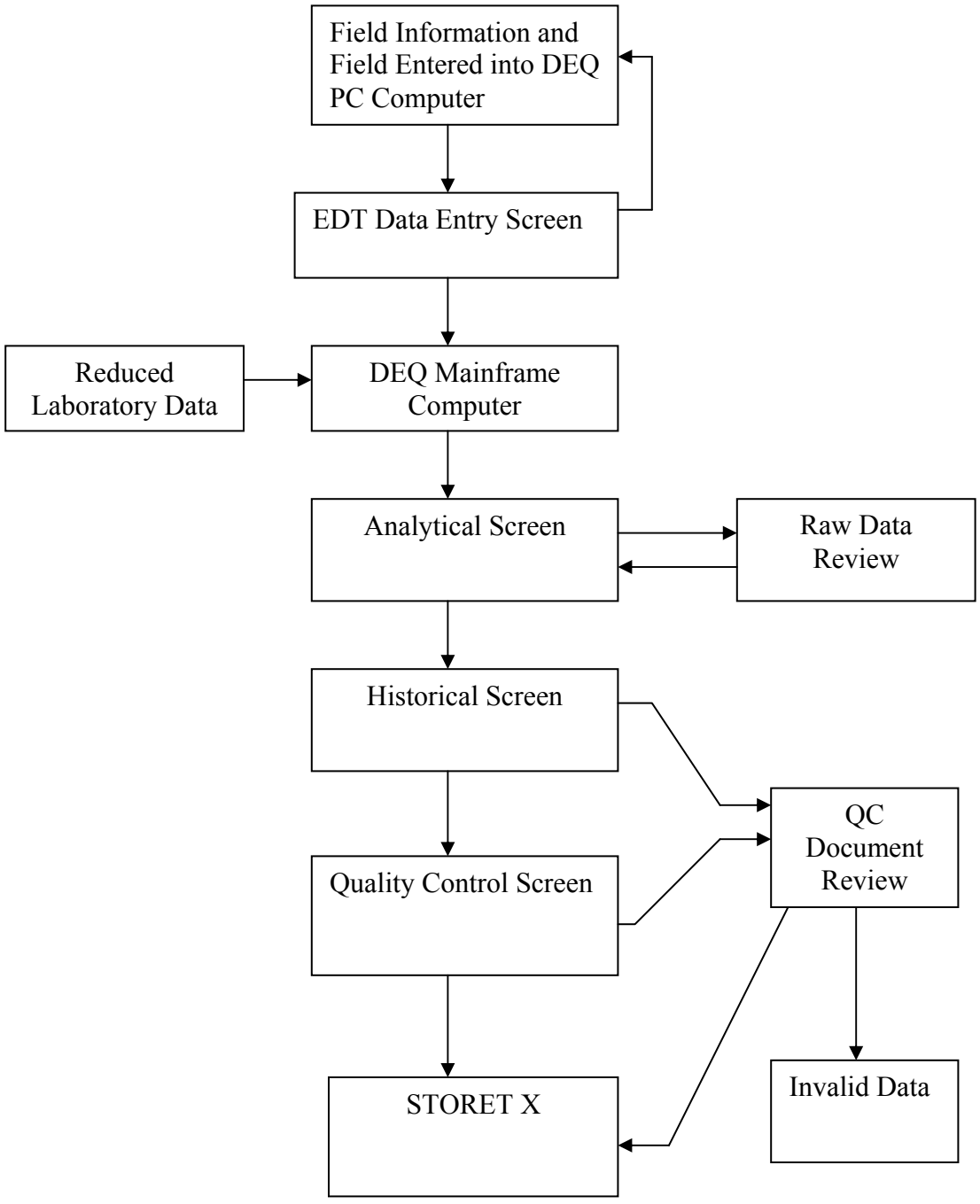
D.2.2 Analytical Screen

Data limits for this initial screening have been established for each parameter based upon analytical reporting limits. These limits are used to identify outliners and data, which are within the described detection limit for each parameter. Upper limits have been set for those parameters such as pH analyses where the analytical method defines an upper detection limit. In addition, a "parts < whole" check is performed on the data where fractions and total parameter determinations are made, such as for solids analyses.

D.2.3 Historical Screening

For the historical screening, parameter limits have been established using historical ambient data. Criteria developed for historical parameter values are used to identify outliners and data, which are within the established ranges for each parameter.

Figure 3 AWQM DATA VALIDATION



Specific sampling site and seasonal variables as the database will further delimit these ranges and computer availabilities allow. Ranges of data variation will be further demarcated using relevant geographic and environmental considerations and appropriate statistical analysis.

D.2.4 Quality Control Sample Screening

5% of the samples summited to DCLS will be quality control samples (field replicates). Results from these quality control samples will be used to establish control limits for the validation system. Because of the volume of data generated and complexity of the validation process, an appropriate computer system and software must be used to implement the data validation system.

For the QC screen, field blanks and field replicate data will be collected in order to develop background information. Appropriate statistical analysis will then be used develop an acceptable range of parameter variation for field blanks and field replicates. For replicate samples, the precision can be expected to vary with concentration. The relative percent difference will be used to develop acceptable ranges for each parameter. Where necessary these ranges will be grouped according to concentration to facilitate comparisons. When the QC sample screen is operational, the analytical and historical screens will be further validated by comparison of QC sample results with established parameter ranges for field blanks and field replicates.

D3 Reconciliation with User Requirements

Outliners that are identified during the screenings go through an evaluation sequence to examine possibly compromised data. A review of field and laboratory documentation is conducted for data exceeding the established control limits. Field notes and laboratory bench sheets associated with outliners are reviewed in order to determine if the data should be invalidated. For data failing the analytical screen, laboratory documentation is reviewed. For data exceeding limits set for the historical and quality control sample screen, The DEQ staff reviews field and laboratory documentation.

When quality control screens and documentation reviews provide evidence of questionable data, The outliners will be rejected and not entered into STORET X system. Rejected data will be retained. Where appropriate, The regional office will initiate corrective action to address the reason for rejection.